

# GAS-STORAGE CARBONS PREPARED BY ALTERNATING OXYGEN CHEMISORPTION AND THERMAL DESORPTION CYCLES

Marek A. Wójciewicz, Brian L. Markowitz, Girard A. Simons\*, and Michael A. Serio

Advanced Fuel Research, Inc., 87 Church Street, East Hartford, CT 06108-3742

\*Simons Research Associates, 3 Juniper Road, Lynnfield, MA 01940-2416

**Keywords:** gas storage, activated carbon, chemisorption, desorption

## ABSTRACT

The desirable characteristics of activated carbons for gas-storage applications are: (1) high microporosity (pores smaller than 2 nm); and (2) low voidage in the storage container (e.g., the use of shaped sorbent elements). A transient chemisorption-desorption char activation technique was used to maximize micropore formation and minimize mesoporosity. Several carbons were prepared at different degrees of burn-off, and the BET surface areas were found to be up to 2000 m<sup>2</sup>/g. The carbons were prepared in the form of pellets to show that the future use of shaped elements can lead to the reduction of voidage in the storage container by up to 40%. The adsorption isotherms of the produced carbons showed high microporosity and no appreciable mesoporosity, even at high burn-offs.

## INTRODUCTION

Gas storage by adsorption on activated carbon is possible at relatively low pressures using activated carbons with a well developed microporosity, i.e., with pores whose radius,  $r_p$ , is less than  $r_{\text{lim}} \approx 10 \text{ \AA}$ . The generation of microporosity requires a uniform surface phenomenon, such as steady-state gasification in the limit of kinetic control or an alternating adsorption-desorption process in which a reactant gas is chemisorbed on the active sites of a carbon surface and then allowed to desorb, removing the carbon from the walls of the pores [1,2]. A model was presented [3] to describe pore growth in microporous carbons and was used to relate the potential micropore volume to the characteristics of the starting material (initial char). Modeling results show that the microporosity can be maximized by choosing an initial char with minimum initial open porosity and significant initial blind porosity within angstrom-size pores. As a spatially uniform surface recession may be obtained via char gasification in the limit of kinetic control, the microporosity-evolution model [3] has been coupled to a pore structure/pore-transport model [4] capable of describing the simultaneous action of diffusive and kinetically-controlled processes. The integrated model [5] was used to determine the conditions under which diffusion-control may be avoided and the char microporosity maximized. Predicted steady-state activation times are extreme for millimeter-size particles (10<sup>4</sup> hours), and faster processes are sought. One such process is that of alternating oxygen chemisorption and desorption [1,2]. Rapid adsorption of oxygen onto the char surface in the absence of desorption (via low-temperature chemisorption), followed by rapid high-temperature desorption in the absence of oxygen, may be used to cyclically remove carbon from the walls of the pores.

In this paper, theoretical analysis of the cyclic chemisorption-desorption process is carried out to assess the time scales of: (1) the oxygen chemisorption step; and (2) the thermal desorption of surface oxides. In addition to the results of the modeling effort, microporosity evolution is reported for chars prepared using the above activation technique.

## MATERIALS AND EXPERIMENTAL TECHNIQUES

A sample of granular polyvinylidene chloride (PVDC), provided by Solvay Polymers, Inc., Houston, Texas, was used as a carbon precursor. PVDC was first pressed into pellets, using a ten-ton press, and then subjected to carbonization. The initial dimensions of the pellets were 13 mm in diameter and ~5 mm in thickness, and the initial weight of each pellet was approximately one gram. The PVDC-carbonization procedure consisted of the following steps: (1) heating from room temperature to 170 °C at 5 °C/min; (2) heating to 230 °C at 0.1 °C/min; (3) heating to  $T_f = 900 \text{ °C}$  at 2 °C/min; (4) holding at  $T_f$  for time  $\tau_f = 240 \text{ min}$ ; and (5) cooling down to room temperature at -22 °C/min. After carbonization, the samples were activated to the desired degree of burn-off using a thermogravimetric analyzer (TGA), and the following routine was performed cyclically: (1) purging the system at 200 °C for 17 minutes in helium; (2) heating at 100 °C/min to  $T_a = 900 \text{ °C}$  (He); (3) holding for 5 minutes (He); (4) cooling at -22 °C/min to  $T_{ch} = 200 \text{ °C}$  (He); and (5) switching from the flow of helium to oxygen and holding for  $\tau_{ch} = 15 \text{ minutes}$  in O<sub>2</sub>. At specified levels of burn-off, samples were taken out of the TGA, weighed, and nitrogen adsorption isotherms were determined using a Micromeritics Digisorb 2600 analyzer.

## RESULTS AND DISCUSSION

### Modeling of the Kinetics of Oxygen Chemisorption and Surface-Oxide Desorption

The primary limitation of the adsorption process is the time required for oxygen to reach the smallest pores in the char. The high chemisorption rate will generate large oxygen gradients within the particle, but diffusion along these gradients is still responsible for delivering the oxygen to the smallest pores. A model has been developed to describe this transient chemisorption process. A chemisorption "front", coupled with gas-phase diffusion, progresses into the pore structure and deposits chemisorbed oxygen on carbon active sites. This model has been used to determine the time required for complete chemisorption of oxygen onto the walls of the smallest pores.

For phenol-formaldehyde char, chemisorbed oxygen loadings of the order of 12 mg O<sub>2</sub>/g C were obtained at 300 °C in one atmosphere of oxygen [6]. The chemisorption time was about 80 minutes, the BET surface area of the char was about 400 m<sup>2</sup>/g C, and the char particle diameter was of the order of 100 microns. A primary concern is how the chemisorption time scales with particle size and oxygen partial pressure. The model described above has been used to predict this scaling. If  $s_p$  represents the internal surface area of the carbon (m<sup>2</sup>/g C), and  $\sigma_w$  represents the chemisorbed oxygen loading per unit surface area (g O<sub>2</sub>/m<sup>2</sup>), then  $s_p\sigma_w$  is the chemisorbed oxygen loading in g O<sub>2</sub>/g C. Oxygen loadings of the order of 12 mg/g and an internal surface area of 400 m<sup>2</sup>/g are consistent with surface loadings ( $\sigma_w$ ) of  $3 \times 10^{-9}$  g/cm<sup>2</sup>. Using this set of chemisorption parameters, model predictions for the chemisorption times are illustrated in Figure 1. In the limit of kinetic control (small particles), increased gas pressure significantly reduces the chemisorption time. However, in the limit of diffusion control (large particles), increased gas pressure does not enhance diffusion. It is clear that operating in one atmosphere of oxygen on up to 7 mm particles will maintain chemisorption times of the order of one hour.

The desorption process is just the reverse from the adsorption process. A desorption "front," coupled with gas phase diffusion and viscous convection, progresses into the pore structure and desorbs the oxygen from the carbon active sites. As the particle temperature is raised, the internal gas pressure increases and viscous convection of the gas from the pore structure becomes rate limiting. This is illustrated in Figure 2. Internal gas pressures in excess of a few hundred pounds per square inch are sufficient to create desorption times less than one tenth of an hour per cycle for centimeter-size particles. As the desorption temperature, and therefore pressure, may be arbitrarily increased, the alternating chemisorption-desorption process is readily limited by the chemisorption step. As each chemisorption-desorption cycle will chemisorb only ~12 mg O<sub>2</sub>/g C, and desorption will remove only 9 mg carbon per gram of carbon, up to 100 cycles may be required to fully activate the carbon. As temperature cycling may require less than one hour per cycle, it is apparent that this activation process is much faster than kinetically controlled gasification and may be used to activate particles up to one centimeter in diameter on time scales of the order of 100 hours.

### Preparation and Characterization of Gas-Storage Carbons

An important consideration in gas-storage applications is the degree of sorbent packing within the storage container. To achieve maximum volumetric storage density, the voidage in the container needs to be minimized. Although some amount of voidage is desirable to ensure adequate gas transport within the sorbent-filled container, the 30-40% voidage typical of randomly packed particles is excessive. Thus, an ideal gas-storage system would consist of a nearly 100% microporous sorbent in the form of tightly packed, shaped elements, e.g., discs 5-10 mm in thickness.

The traditional char-activation methods, which are based on steady-state carbon gasification, usually lead to pore-mouth widening and to the creation of the undesirable mesoporosity. The problem is caused by mass-transfer limitations that occur within the char particle, and this phenomenon is increasingly more severe for particles of larger sizes. Thus, the steady-state activation methods are incapable of producing large elements of highly microporous sorbent. This is in contrast to the cyclic chemisorption-desorption method, which, by obviating the mass-transfer limitations, should allow to obtain large elements of microporous sorbent. This presumption is tested below by analyzing the pore structure of sorbent pellets activated using the cyclic method.

Adsorption isotherms of the PVDC char pellets activated to different burn-offs are shown in Figure 3. It is evident that all the curves have the shape of a Type I isotherm, which is characteristic of highly microporous materials [7]. It is remarkable that even the pellets with as much as 87% burn-off do not show mesopore formation (transition to a Type IV isotherm).

Although the BET surface-area analysis is not quite applicable to highly microporous materials [7], the results can nevertheless serve as an index of sample microporosity. In other words, BET surface areas reported for microporous solids will not have physical meaning, but larger values will indicate a higher degree of microporosity. Another measure of microporosity is the micropore volume evaluated using the Dubinin-Radushkevich equation [8,7]. BET surface areas and micropore volumes of the PVDC char pellets are presented in Figure 4. It can be seen that both variables increase with the increasing burn-off, which indicates that the sorbent becomes more and more microporous as activation progresses.

Additional insights into the morphology of sorbent pellets can be provided by Scanning Electron Microscopy (SEM). SEM pictures of an activated PVDC char pellet are shown in Figure 5. It can be seen the PVDC granules that were initially present within the pellet have changed their original spherical shape (uncompressed PVDC polymer) to a more pentagonal or hexagonal pattern (PVDC char pellet). These particles have an approximate size of 170 microns. The change in particle shape drastically decreases the ~40% voidage typically found in spherical particles. Another interesting observation is the 5-10 micron spaces between individual granules within each pellet. It is expected that these spaces will make gas transport into and out of the storage container far less restricted than in the case of "solid" pellets. Preliminary calculations carried out for the above material show that mass transfer within a bed of shaped sorbent elements should not be a serious problem for gas-storage applications. A more detailed analysis of this result will be discussed in a future publication.

Figure 5 also shows one-micron pits, which are most likely formed during the evolution of pyrolysis gas. Modifications in the PVDC pyrolysis routine may lead to a change in the size and the number of these structural features.

## CONCLUSIONS

- Theoretical analysis of the cyclic chemisorption-desorption process shows that char particles up to one centimeter in size can be activated on time scales of the order of 100 hours.
- All PVDC-derived carbons, activated to burn-offs of up to 87% using the cyclic technique, were found to exhibit Type I adsorption isotherms. This is indicative of a high degree of microporosity. Nitrogen BET surface areas and Dubinin-Radushkevich micropore volumes were found to be up to 2000 m<sup>2</sup>/g and 0.84 cm<sup>3</sup>/g, respectively. It can be concluded that the concept of producing large, shaped elements of microporous carbon has been experimentally validated. This finding is associated with the benefit of an increased volumetric storage density (by up to 40%) due to improved sorbent packing. First tests of hydrogen-storage capacity of the above sorbents have been carried out, and the results look very encouraging [2].
- SEM micrographs show that sorbent pellets are composed of nested pentagonal or hexagonal particles about 170  $\mu$ m in size. Spaces between the particles are 5–10  $\mu$ m wide, and they should provide a good medium for hydrogen transport without creating excessive voidage.

## ACKNOWLEDGMENTS

This research was supported by the NASA Johnson Space Center under SBIR contract No. NAS9-19470. The authors also acknowledge helpful comments contributed by Dr. David F. Quinn of the Royal Military College of Canada and Professor Eric M. Suuberg of Brown University.

## REFERENCES

- 1 Quinn, D. F. and Holland, J. A., U.S. Patent No. 5,071,820, 1991
- 2 Wójtowicz, M. A., Smith, W. W., Serio, M. A., Simons, G.A. and Fuller, W. D., in *Carbon '97* (Ext. Abstr. 23rd Biennial Conf. Carbon), The Pennsylvania State University, State College, PA, 1997, vol. I, pp. 342-343
- 3 Simons, G. A. and Wójtowicz, M. A., in *Carbon '97* (Ext. Abstr. 23rd Biennial Conf. Carbon), The Pennsylvania State University, State College, PA, 1997, vol. I, pp. 328-329.
- 4 Simons, G.A., in *Nineteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 1982, pp. 1067-1076.
- 5 Simons, G. A. and Wójtowicz, M. A., in *Proc. 9th Int. Conf. on Coal Science*, DGMK, Hamburg, Germany, 1997, pp. 1783-1786.
- 6 Wójtowicz, M. A., *Thermogravimetric Study of Active Sites in the Process of Low-Temperature Oxidation of Char*, Ph.D. thesis, Brown University, Providence, RI, 1988.
- 7 Gregg, S. J. and Sing, K. S. W., *Adsorption, Surface Area and Porosity*, Academic Press, London, 1982.
- 8 Dubinin, M. M. and Radushkevich, L. V., *Proc. Acad. Sci. USSR* **55**, 331, 1947; Dubinin, M. M., *Russ. J. Phys. Chem.* **39**, 697, 1965.

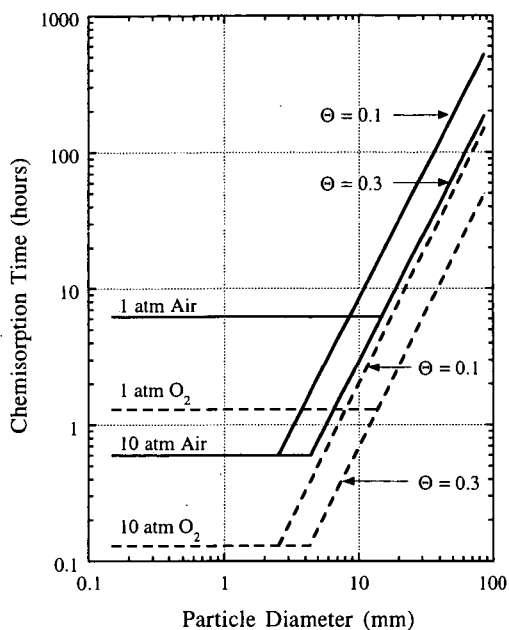


Figure 1. Scaling of chemisorption time with particle size and gas pressure (phenol-formaldehyde resin char carbonized at 1000 °C for 2 hours;  $\Theta$  is char porosity).

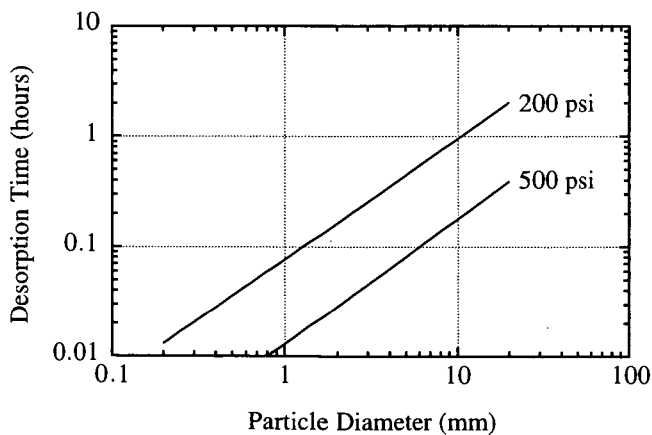


Figure 2. Scaling of desorption time with particle size and internal gas pressure (convection limited, 200 psi and 500 psi).

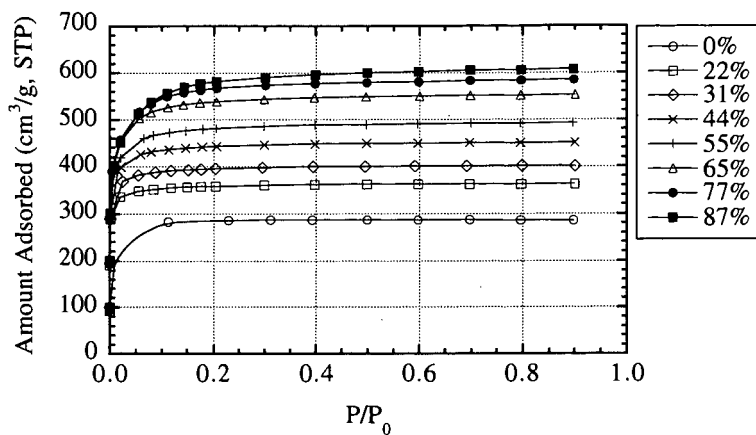


Figure 3. Nitrogen adsorption isotherms for PVDC-char pellets activated to various degrees of burn-off.

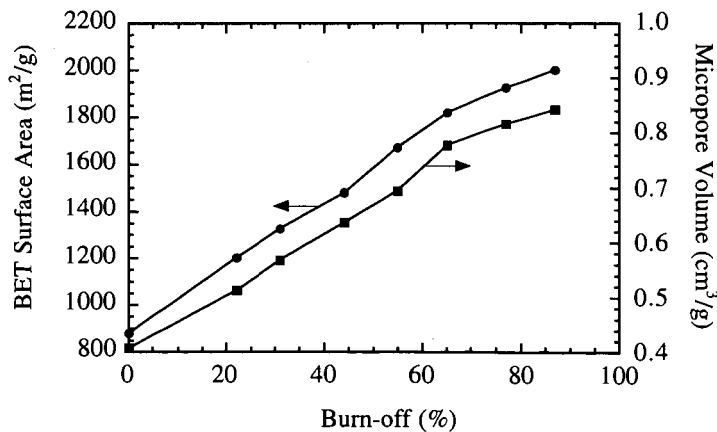


Figure 4. Nitrogen BET surface area and Dubinin-Radushkevich micropore volume versus per cent burn-off for PVDC char pellets.

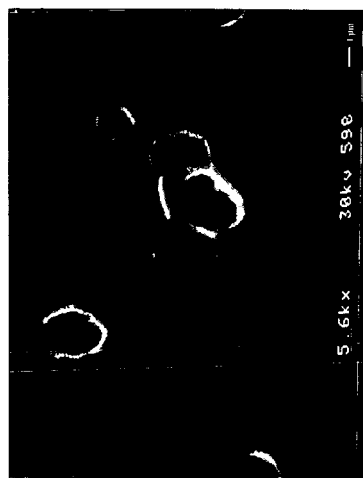
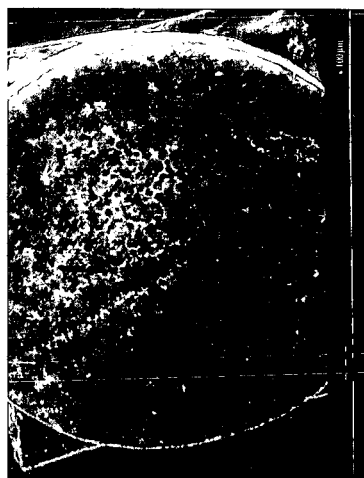
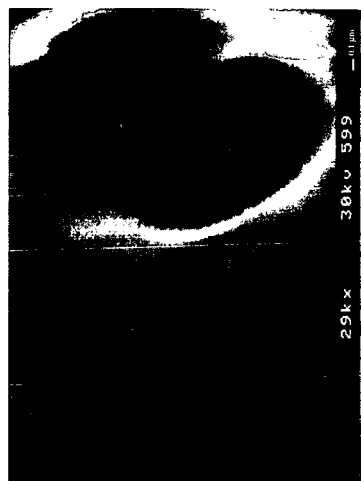
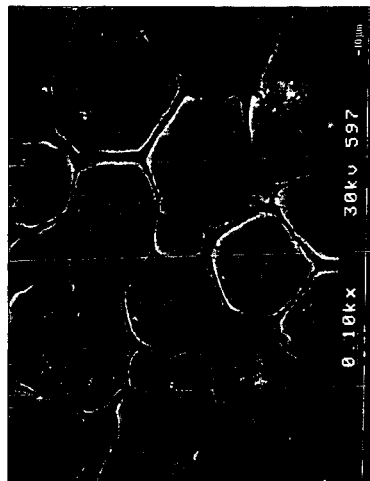


Figure 5. SEM micrographs of a PVDC char pellet ( $T_i = 905^\circ\text{C}$ ,  $\tau_i = 5\text{ min}$ ,  $T_{ch} = 200^\circ\text{C}$ ,  $\tau_{ch} = 15\text{ min}$ ,  $T_c = 900^\circ\text{C}$ ,  $BO = 64\%$ ).